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Brilliant Blue FCF degradation by persulfate/zero valent iron: the effects of influencing parameters and anions

Maryam Yousefi[a], Farshid Ghanbari[b,c], Mohammad Ali Zazouli[d], Soheila Madihi-Bidgoli[e,*]

[a]*Student Research Committee, Mazandaran University of Medical Sciences, Sari, Iran*
[b]*Environmental Technologies Research Center, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran*
[c]*Student Research Committee, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran*
[d]*Department of Environmental Health Engineering, Health Sciences Research Center, Faculty of Health, Mazandaran University of Medical Sciences, Sari, Iran*
[e]*Division of Food Safety, Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran, Tel. +989104956879; email: s.madihi8@gmail.com*

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ABSTRACT

In this study, zero valent iron (ZVI) was applied as an activator for persulfate (PS) to degrade a food dye (Brilliant Blue FCF) from aqueous solutions. The effect of pH, PS concentration, ZVI dosage and initial dye concentration was evaluated. The degradation efficiency was obtained about 98.8% under optimum conditions, i.e., pH of 3, ZVI dosage of 0.5 g/L, PS dosage of 4 mM and initial dye concentration of 20 mg/L. PS had higher decolorization rate compared with H_2O_2 and percarbonate. Chemical oxygen demand and total organic carbon removal efficiencies were about 45.3% and 36.6%, respectively. Among anions, phosphate and bicarbonate showed an inhibitory effect on the decolorization of the dye. Moreover, quenching experiments exhibited that sulfate radical is major agent of oxidizing the dye. According to the results, PS/ZVI process could be an effective approach to pollutant degradation.

Keywords: Brilliant Blue FCF; Zero valent iron; Persulfate; Sulfate radical; Food dye

1. Introduction

Dyeing wastewater contains a considerable amount of dyes that may be toxic, mutagenic and carcinogenic to human and animals. Besides the impact on health, dyes can be a particularly serious threat to aquatic environment [1,2]. The presence of dye and color-causing agents has always been unpleasant in water for consumers. Nowadays, we must not be surprised at this issue that color also can be recognized as water pollutant. Therefore, an increasing attention has been paid to the decolorization of industrial wastewaters [3,4].

Brilliant Blue FCF (BBF) is a synthetic dye which is classified as a triarylmethane dye. It is a colorant for foods and applied in ice cream, dairy products, soaps, shampoos and mouthwash. Furthermore, it is utilized in hydrological tracing to visualize infiltration and water distribution in the soil [5–7]. BBF induces neurological and reproductive disorders; it can also cause blood lymphoma and allergic reactions in individuals with pre-existing moderate asthma. It causes acute oral toxicity in animals. In this way, it has been reported that LD_{50} of BBF in mice and rats >2,000 and 4,600 mg/kg, respectively [5,8,9]. Keeping up all these points, it is necessary to find a new method for removal of BBF from water resources before being discharged into water bodies. Conventional methods such as coagulation and adsorption techniques have been investigated in numerous studies for color removal from contaminated water [10,11]. Chemical oxidation processes has been taken a much consideration as an effective method for

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[*] Corresponding author.

the decolorization of dyes. Advanced oxidation processes (AOPs) involve the generating highly reactive radicals in sufficient quantity to degrade organic pollutants [12,13]. In recent years, sulfate radical-based AOPs have received a considerable attention as promising methods to degrade toxic and persistent pollutants. The sulfate radical is a powerful oxidant with redox potential of 2.5–3.1 V which can be produced through activation sulfate-based oxidants such as persulfate (PS) and peroxymonosulfate [14,15]. The PS anion is a strong oxidant with oxidation potential of $E^0 = 2.01$ V which are responsible for degradation of a wide range of contaminants in in situ chemical oxidation in groundwater remediation [16]. It can be also activated in different methods including ultrasonic, heat [17], transition metal ions [18], electrochemical process [19] and ultraviolet [16]. In order to activation of PS some metals have been investigated in which silver and iron ions have been successfully applied for the activation of PS [20]. Zero valent iron (ZVI) has recently become the most common metallic reducing agent for environmental remediation due to its abundance, low toxicity, low cost, high reactivity and effectiveness [15,21]. However, ZVI has been widely used as catalyst for the decomposition of H_2O_2 in Fenton-like process in decontamination of wastewater [21].

ZVI can be used as an activator for PS for the production of sulfate radicals. ZVI can produce iron ions in PS/ZVI system based on reaction of the oxidizing ZVI by water and PS [22,23].

$$\mathrm{Fe^0 \rightarrow Fe^{2+} + 2e^-} \tag{1}$$

$$\mathrm{Fe^0 + S_2O_8^{2-} \rightarrow Fe^{2+} + 2SO_4^{2-}} \tag{2}$$

$$\mathrm{Fe^{2+} + S_2O_8^{2-} \rightarrow SO_4^{\bullet -} + Fe^{3+} + SO_4^{2-}} \tag{3}$$

Moreover, the presence of Fe^0 can reduce ferric ion produced to ferrous ion and propagate reaction chains to produce sulfate radical consequently [24].

$$\mathrm{Fe^0 + 2Fe^{3+} \rightarrow 3Fe^{2+}} \tag{4}$$

In addition, heterogeneous activation of PS may occur in the surface of ZVI based on Eq. (5) [25]:

$$\mathrm{Fe + 2S_2O_8^{2-} \rightarrow 2SO_4^{\bullet -} + Fe^{2+} + 2SO_4^{2-}} \tag{5}$$

In fact a combination of homogenous and heterogeneous reactions activates PS to generate sulfate radical as oxidative agent to destruct organic compounds.

In this study, the effects of pH, PS and ZVI dosages, initial dye concentration were investigated on BBF degradation. The effects of some anions (nitrate, bicarbonate, phosphate and chloride) were studied on the performance of the system. Moreover, reducing organic compounds of BBF was studied based on total organic carbon (TOC) and chemical oxygen demand (COD) removal efficiencies. Finally, reaction mechanism was determined by quenching experiments.

2. Materials and methods

2.1. Chemicals

BBF ($C_{37}H_{34}N_2Na_2O_9S_3$) was purchased from Alvan Sabet (Iran) with the purity of 99%. The properties of BBF are presented in Table 1. Sodium persulfate ($Na_2S_2O_8$; Merck Inc., Germany) was used as the source of PS anion. Hydrogen peroxide and sodium percarbonate were purchased from Aldrich Company (USA). ZVI was purchased from Sigma-Aldrich Company (USA) with purity of 99% and size of 325 mesh. The sodium hydroxide, sulfuric acid, sodium bicarbonate, sodium chloride, sodium phosphate and sodium nitrate were purchased from Samchun Company (South Korea). Benzoic acid (BA) and *tert*-butyl alcohol (TBA) were obtained from Fluka Inc. (Switzerland). All solutions were prepared by deionized water.

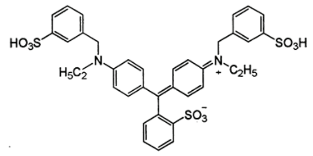
2.2. Experiments of BBF degradation

All experiments were conducted in 500 mL batch reactor (flask) at 25°C. 300 mL of the dye solution was used for the evaluation of ZVI/PS process. A certain amount of ZVI was added to the solution. Afterward, the specific dosage of different PS concentrations was loaded to the solution. The solution pH was adjusted by sulfuric acid to desired level. Then, the flasks were placed on the shaker with 250 rpm. At selected time intervals, a known amount of aliquot was withdrawn from the flask for dye measurement. The experiments of percarbonate and hydrogen peroxide were carried out similar with ZVI/PS system. The color measurements were immediately determined by a spectrophotometer. The samples were quenched by sodium thiosulfate for the measurement of COD and TOC. Scavenging experiments were conducted with adding the chemical probes (BA and TBA) similar to main experiments.

2.3. Analytical methods

The BBF concentrations in the solutions were determined using a spectrophotometer (DR5000, Hach, USA) at the wavelength of 628 nm as maximum absorption wavelength. TOC was analyzed by a TOC analyzer (Shimadzu, Japan). COD values were determined by colorimetric method by a

Table 1
Characteristics of Brilliant Blue FCF

Dye	Brilliant Blue FCF
Structure	
Chemical formula	$C_{37}H_{34}N_2Na_2O_9S_3$
E number	E133
Color index No.	42090
Molecular weight (g/mol)	792.85
CAS No.	3844-45-9

spectrophotometer at the wavelength of 420 nm [26]. The accuracy of TOC and COD values was checked by potassium hydrogen phthalate. PS, hydrogen peroxide and percarbonate were measured by iodometric method [27].

3. Results and discussion

3.1. Effect of the solution pH

The pH effect on dye removal was investigated at the pH = 2–6 under the conditions of ZVI dosage of 0.5 g/L, PS dosage of 1 mM and initial dye concentration of 20 mg/L. As can be seen in Fig. 1, the degradation efficiency of BBF was obtained about 66.1%, 72.3%, 58.8%, 44.9% and 36.9% in pH = 2.0, pH = 3.0, pH = 4.0, pH = 5.0 and pH = 6.0, respectively.

As a result, the removal efficiency of BBF in PS/ZVI system was accelerated at the pH of 3.0. The reduction yield at the higher pH than 3 can be attributed to the precipitation of Fe^{2+} and Fe^{3+} decreasing the amount of iron ions. Moreover, sulfate radical in acidic condition has higher oxidation potential [22]. At the strong acidic condition (pH = 2.0), decolorization was reduced. The excess hydrogen ions at acidic condition scavenge sulfate radicals according to Eq. (6) [28].

$$SO_4^{\bullet-} + H^+ + e^- \rightarrow HSO_4^- \tag{6}$$

Hence, pH = 3.0 was considered for subsequent experiments for ZVI/PS system in which pH = 3.0 has been reported as suitable pH in Fenton-based processes by H_2O_2 and PS [12,19].

3.2. Effect of persulfate dosage

Fig. 2 displays the effect of PS dosages on the BBF removal. Different concentrations of PS (in the range of 0–8 mM) were applied under conditions: pH = 3, reaction time = 30 min, ZVI dosage = 0.5 g/L, and BBF concentration = 20 mg/L. In the absence of PS, decolorization efficiency was 22.3% which can be related to the adsorption of the dye on the surface of ZVI and production of ferrous ion from ZVI as coagulant agent agglomerating the dye. Color removal efficiencies were 50.2%, 72.3%, 83.6%, 98.9% and 80.4% in the presence of 0.5, 1, 2, 4 and 8 mM of PS dosage, respectively. According to the results, increase of PS concentration to 4 mM led to increase of color removal. The higher concentrations of PS as an oxidant agent resulted in more production of sulfate radical and enhancement of the degradation rate consequently. It was observed a decrease in decolorization at PS concentration of 8 mM, this result was in accordance with the finding of phenol removal by electro-persulfate conducted by Rahmani et al. [29]. Further increase in PS dosage leads to scavenging of sulfate radical by $S_2O_8^{2-}$ based on Eq. (7) [29,30].

$$SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet-} \tag{7}$$

3.3. Effect of ZVI dosage

The effect of activator dosages on the performance of PS/ZVI system was investigated at ZVI dosages ranging from 0 to 1 g/L and their results presented in Fig. 3. In this work, the optimum ZVI dosage for the discoloration of BBF was 0.5 g/L. In the absence of ZVI, sole PS could degrade 18.3% of BBF during 30 min. This efficiency is related to this fact that PS is a strong oxidant destructing organic compounds.

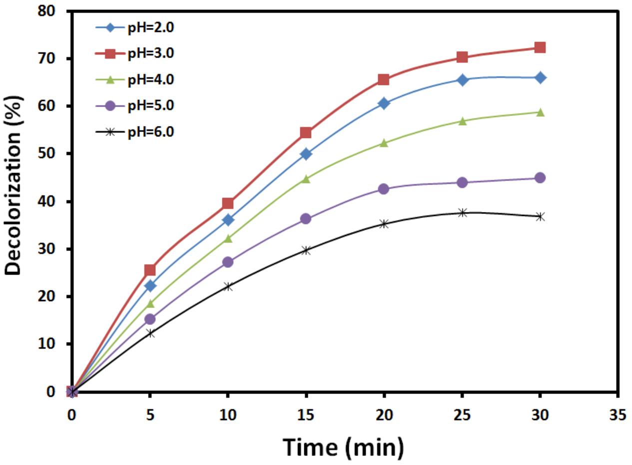


Fig. 1. The effect of initial pH on BBF removal in PS/ZVI system (ZVI dosage = 0.5 g/L, PS dosage = 1 mM and initial dye concentration = 20 mg/L).

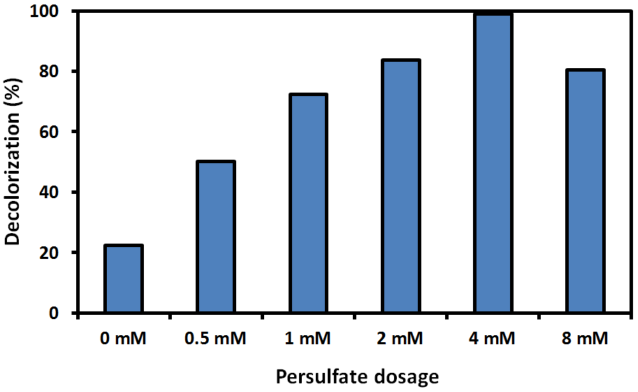


Fig. 2. The effect of persulfate dosages on BBF removal in the PS/ZVI system (pH = 3.0, reaction time = 30 min, ZVI dosage = 0.5 g/L and initial dye concentration = 20 mg/L).

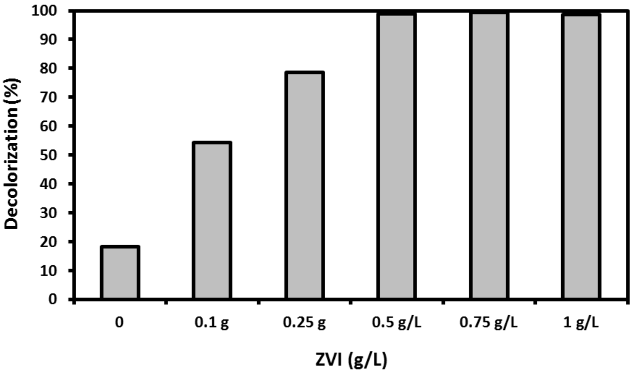


Fig. 3. The influence of ZVI dosage on removal of BBF in the PS/ZVI process (pH = 3, reaction time = 30 min, PS dosage = 4 mM and initial dye concentration = 20 mg/L).

Moreover, the sole application of PS in acidic condition can produce sulfate radical through acid decomposition based on Eqs. (8) and (9) [31,32].

$$H^{+} + S_2O_8^{2-} \rightarrow HS_2O_8^{-} \quad (8)$$

$$HS_2O_8^{-} \rightarrow SO_4^{\bullet -} + SO_4^{2-} + H^{+} \quad (9)$$

With the increase of ZVI dosage from 0.1 to 0.5 g/L, decolorization was increased from 54.3% to 98.9%. Increasing in ZVI resulted in more production of ferrous ion as activator and higher generation of sulfate radical as a consequence. Increasing the ZVI dosage more than 0.5 g/L had no significant effect on the degradation efficiency. The same finding was observed about degradation of *p*-chloroaniline in PS/ZVI process by Hussain et al. [22,25]. As can be seen, excess ZVI dosage had no scavenging effect (Eq. (10)) for sulfate radical which can be superior compared with ferrous ion application.

$$Fe^{2+} + SO_4^{\bullet -} \rightarrow Fe^{3+} + SO_4^{2-} \quad (10)$$

3.4. Effect of dye concentration

The effect of different initial dye concentration in PS/ZVI system has been presented in Fig. 4(a). With increasing of the dye concentration, the degradation efficiency decreased. In higher concentration of the dye, the BBF molecules in the solution enhanced while the concentrations of oxidative agents were constant. In this way, decolorization significantly dropped in higher concentration. Therefore, reduction in efficiency is attributed to the insufficient amount of ZVI, PS and sulfate radicals as the main responsible of decolorization. In addition, the generation of the intermediate compounds in higher dye concentration might lead to competitive reaction between dye molecules and intermediates with sulfate radicals. Hence, the decolorization rate is declined with increasing the dye concentration [33]. The first-order kinetic model was fitted for BBF degradation by ZVI/PS process based on Eq. (11) and their rate constants are presented in Fig. 4(b).

$$-\mathrm{Ln}\frac{\left[\mathrm{dye}_{\mathrm{BBF}}\right]}{\left[\mathrm{dye}_{\mathrm{BBF}}\right]_0} = kt \quad (11)$$

It can be seen that with the increase of initial dye concentration, rate constant decreased significantly. In this manner, rate constants were 0.2024, 0.144, 0.057, 0.0262 min^{-1} for initial dye concentrations of 10, 20, 50 and 100 mg/L, respectively. These results showed that the concentration of pollutant is critical factor in ZVI/PS system.

3.5. Effect of various inorganic anions

In textile wastewater, the dyes may co-exist with different inorganic substances especially anions which had strong tendency to reaction with free radicals. The effects of some anions (NO_3^-, Cl^-, HCO_3^- and PO_4^{3-}) were studied on decolorization of BBF in ZVI/PS system (Fig. 5(a)). In literature, chloride ions showed both promotional and inhibitory effects in sulfate-radical-based AOPs. In this study, in the presence of chloride, decolorization was slightly decreased. Although chloride accelerates corrosion of ZVI for more production of ferrous ion, chloride can scavenge sulfate radical based on Eqs. (12) and (13) [34,35].

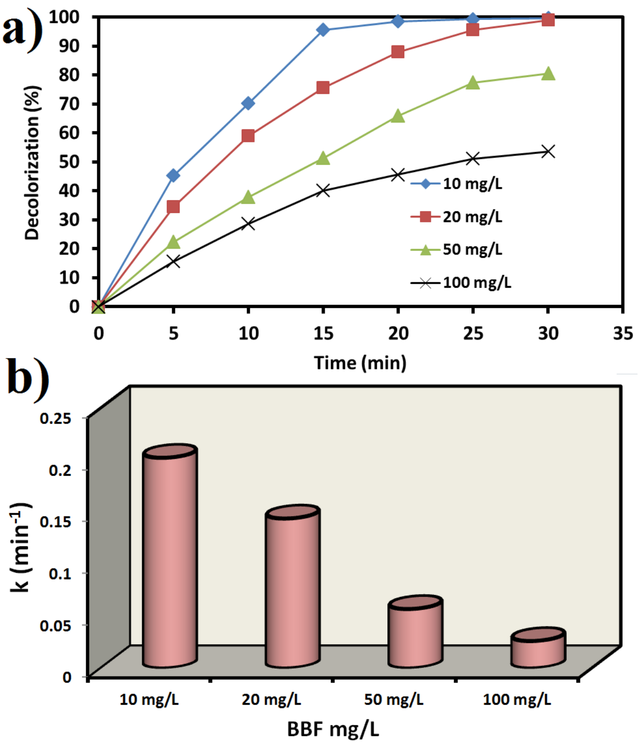


Fig. 4. (a) The effect of initial dye concentration on BBF removal in the PS/ZVI process and (b) rate constants of first-order kinetic model (ZVI dosage = 0.5 g/L, PS dosage = 4 mM and pH = 3.0).

$$SO_4^{\bullet -} + Cl^{-} \rightarrow SO_4^{2-} + Cl^{\bullet} \quad (12)$$

$$SO_4^{\bullet -} + Cl^{\bullet} + Cl^{-} \rightarrow SO_4^{2-} + Cl_2 \quad (13)$$

However, the presence of active chlorine species (HOCl, OCl^- and $Cl^{\bullet}$) can degrade organic compounds. In case of nitrate ions, decolorization was declined markedly resulted from the scavenging of sulfate radicals by nitrate ion according to Eq. (14). Nitrate radical produced is less reactive than sulfate radical [36].

$$SO_4^{\bullet -} + NO_3^{-} \rightarrow SO_4^{2-} + NO_3^{\bullet} \quad (14)$$

It can be found that the degradation efficiency significantly decreased in the presence of bicarbonate and phosphate anions. Bicarbonate ions are recognized as scavenger of free radicals. Bicarbonate and carbonate ions in water can rapidly react with sulfate radicals and produce carbonate radicals with less redox potential (Eq. (15)). Moreover, the presence of carbonate precipitated ferrous ions and so availability of iron for activation of PS was reduced [34,37]. It should be noted that by adding bicarbonate anion, the solution pH increased significantly and reached 6.8.

$$SO_4^{\bullet -} + HCO_3^- \rightarrow SO_4^{2-} + CO_3^{\bullet -} + H^+ \tag{15}$$

The presence of phosphate ions decreased decolorization significantly. Phosphate ions can be adsorbed on the surface of ZVI and prevent PS activation. Phosphate ions can attach surrounding of ZVI and reduce possibility of the reaction of ZVI with PS. Phosphate ions not only scavenge sulfate radicals but also prevent activation of PS [35]. Generally, phosphate and bicarbonate ions are powerful scavengers for sulfate and hydroxyl radicals. Both anions compete with dye molecules for reaction with the radical sulfate.

3.6. Reusability of ZVI

ZVI was used for fifth cycle under the same conditions. ZVI was separated by an external magnet and washed by deionized water for three times and then dried in 75°C for 2 h. Fig. 5(b) illustrates the performance of ZVI in dye decolorization in five-run experiments after the ZVI recycled. As can be seen, decolorization efficiency was noticeability declined after fresh ZVI. In this way, decolorization efficiencies were 98.9%, 84.2%, 74.2%, 60.1% and 48.2% for fresh, second, third, fourth and fifth uses of ZVI. This reduction in efficiency was related to the reduction iron content of ZVI during five cycle uses. Moreover, the surface of ZVI may be contaminated by intermediates [38]. These results indicate that ZVI is a good catalyst for only two cycle uses.

3.7. Comparison of different oxidants

The performance of H_2O_2/ZVI and percarbonate/ZVI systems on BBF removal was evaluated under the same condition of PS/ZVI system and their results are presented in Fig. 6(a). H_2O_2/ZVI and percarbonate/ZVI systems are based on Fenton chemistry with the generation of hydroxyl radical [39,40].

$$Fe^{2+} + H_2O_2 \rightarrow HO^{\bullet} + Fe^{3+} + HO^- \tag{16}$$

As can be seen, the PS/ZVI system had better performance compared with other systems. These results showed that sulfate-radical-based system was more effective than hydroxyl-radical-based systems because the sulfate radical is more selective for oxidation of pollutants [15]. On the other hand, in comparison with percarbonate/ZVI system, H_2O_2 exhibited a high efficiency. Due to the presence of bicarbonate in the structure of percarbonate ($NaHCO_3.3H_2O_2$), competition reactions occurred according to Eqs. (17) and (18) [41,42].

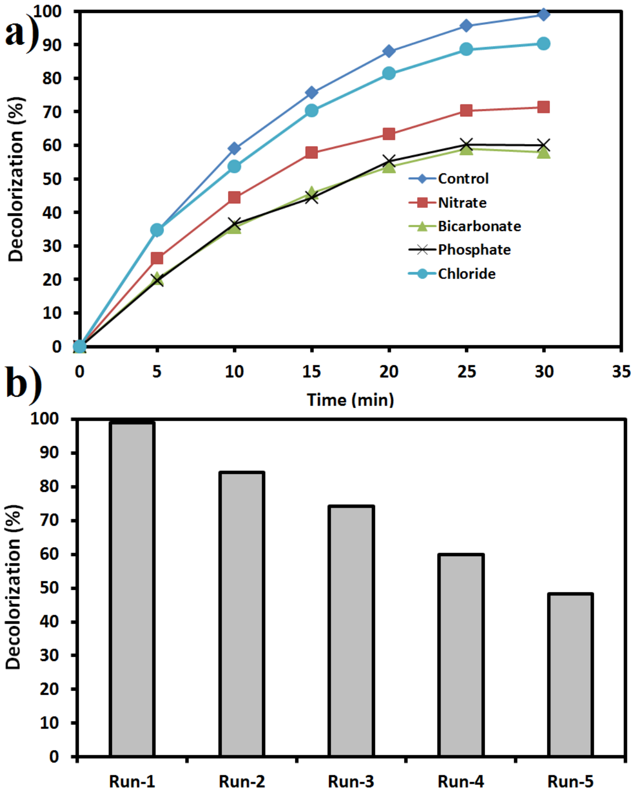


Fig. 5. (a) The effect of anions on BBF removal in the PS/ZVI process and (b) decolorization of BBF in five uses of ZVI catalyst (ZVI dosage = 0.5 g/L, PS dosage = 4 mM, anions concentration = 4 mM and pH = 3).

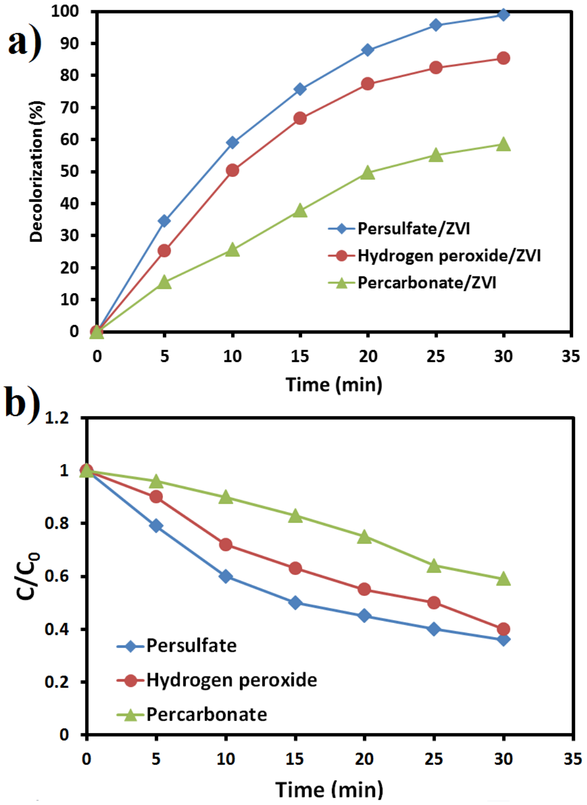


Fig. 6. (a) Comparison of different oxidants/ZVI on BBF removal and (b) oxidant decay in oxidant/ZVI system (ZVI dosage = 0.5 g/L, oxidant dosage = 4 mM and pH = 3).

$$HCO_3^- + HO^\bullet \rightarrow CO_3^{\bullet-} + H_2O \quad (17)$$

$$CO_3^{2-} + HO^\bullet \rightarrow CO_3^{\bullet-} + HO^- \quad (18)$$

In order to confirm the performance of the oxidants, the oxidant decay was monitored during the reaction time in oxidant/ZVI system. Fig. 6(b) presents oxidant decay for three systems. It can be seen that, decay rate of PS was higher than other oxidants indicating more decomposition of PS through activation by ZVI. PS, H_2O_2 and percarbonate decays were 64%, 60% and 41%, respectively. This result confirmed that ZVI was an effective activator for PS compared with H_2O_2 and percarbonate.

3.8. Mineralization and identification of reaction mechanisms

Mineralization of BBF was determined by TOC and COD indices under optimum conditions. The results are indicated in Fig. 7(a). Accordingly, BBF removal efficiency was 98.8% while COD and TOC decay rates obtained about 45.3% and 36.6%, respectively. The significant difference between decolorization and mineralization dye can be attributed to the peresence of three sulfonic acid groups and aromatic rings in the BBF structure. During the oxidation of BBF molecules, sulfonic acid groups decay sooner than aromatic rings that led to accelerate decolorization rate. Therefore, BBF degradation can generate intermediates which decrease the PS/ZVI system efficiency in terms of COD and TOC removals.

In order to determine reaction mechanism, scavenging experiments were carried out by two organic probes including BA and TBA with concentration of 20 mM. BA is an effective quencher for both sulfate and hydroxyl radicals in which rate constants are 1.2×10^9 and 4.2×10^9 $mol^{-1} s^{-1}$ for sulfate radical and hydroxyl radical, respectively [43]. On the other hand, TBA is well known as a powerful scavenger for hydroxyl radical with the rate constant of $(3.8–7.6) \times 10^8$ $mol^{-1} s^{-1}$, while its rate constant with sulfate radical is 1,000-folds less than that with hydroxyl radical [44,45]. Fig. 7(b) shows the effect of presence of the probes in decolorization of BBF. As can be seen, in the presence of BA, decolorization significantly dropped indicating BA could scavenge both radicals. Whereas, in the presence of TBA, decolorization was slightly decreased in a way that decolorization efficiency was 90.2% in 30 min reaction time compared with 98% removal efficiency in control condition. These results illustrated that sulfate radical is the major agent of BBF degradation. It should be noted that the solution pH of 3 has a critical role in high contribution of sulfate radical since sulfate radical reacts with OH^- in pH > 7 and produces hydroxyl radical [30].

4. Conclusions

In this work, the application of ZVI as an activator of PS was investigated in BBF removal. 98.9% decolorization of 20 mg/L BBF occurred under the conditions of 4 mM PS, 0.5 g/L ZVI, 3.0 pH and 30 min reaction time. Rapid decolorization of BBF followed first-order kinetic with rate constant of 0.2024 min^{-1}. In contrast to PS, ZVI had no scavenging effect in excess dosage. The effect of anions showed that phosphate and bicarbonate ions had an inhibitory effect on decolrization of BBF. Moreover, PS exhibited better performance in comparison with H_2O_2 and percarbonate. The low mineralization of BBF degradation indicated possibility of the presence of intemediates. Quenching experiments showed that sulfate radical was the major oxidative agent of BBF degradation. The ZVI/PS system can be considered as a simple and promising process for the degradation of organic pollutant.

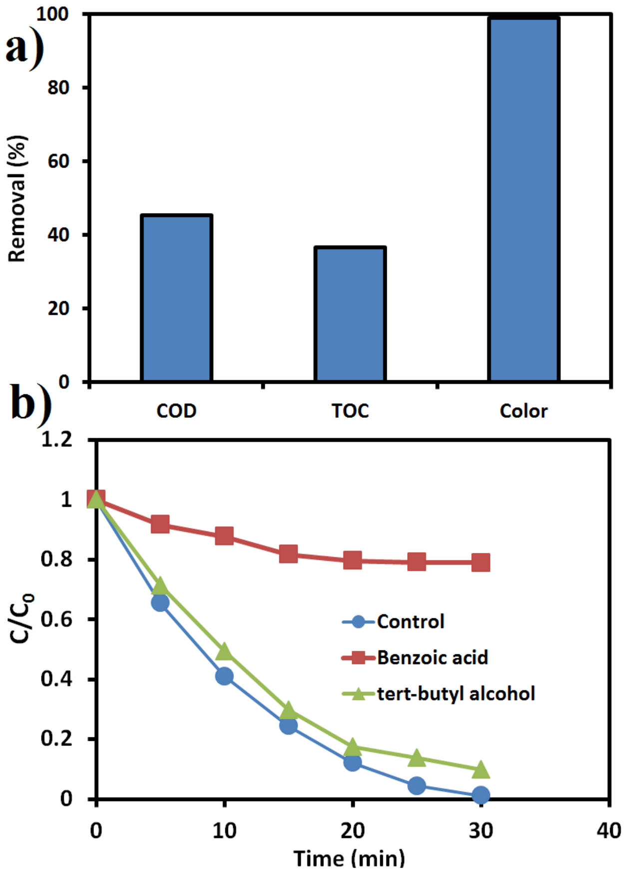


Fig. 7. (a) Mineralization of BBF in ZVI/PS and (b) BBF degradation in the presence of TBA and BA (0.02 M) system (ZVI dosage = 0.5 g/L, PS dosage = 4 mM, pH = 3).

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